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Decolorization of ethyl orange azo dye by oxidation process with acidified chloramine-T: spectrophotometric, kinetic and mechanistic approaches

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ABSTRACT

Ethyl orange (EO) is a mono-azo dye, which is chiefly used as a dye in textile, food, and cosmetic industries. Removal of this dye from wastewater generated by these industries is a main concern in wastewater treatment. Hence, there is a need for a simple and inexpensive method to abolish this dye present in wastewater. A search through literature revealed that very few reports are available on the decolorization of EO dye and also no kinetic and mechanistic studies have been carried out about this dye. Consequently, an attempt is made to develop an oxidative decolorization method for EO dye with chloramine-T (CAT). The present study also aims to investigate the kinetics and mechanism of oxidative decolorization of EO dye with CAT in $HClO_4$ medium spectrophotometrically ($\lambda_{max} = 474$ nm) at 303 K. The reaction exhibits a first-order dependence of rate on $[EO]_o$ and fractional-order dependence, each on $[CAT]_o$ and $[H^+]$, respectively. The dielectric effect is positive. Activation parameters have been deduced. Oxidation products were identified as *N*-(4-diethylamino-phenyl)-hydroxyamine and 4-nitroso-benzenesulfonic acid. Suitable mechanism and related rate law have been worked out. Importantly, the present decolorization method is definitely an advantageous alternative technique in treating the EO dye present in wastewater.

Keywords: Ethyl orange; Chloramine-T; Oxidative decolorization; Kinetics; Mechanism

1. Introduction

The azo dyes contain one or more azo groups, –N=N–, as the primary chromophore. Azo dyes are foremost and vague group of synthetic dyes [1]. Ethyl orange (EO: 4-[4-(diethylamino)-phenylazo]benzenesulfonic acid, sodium salt) is chiefly used in the textile industry for dyeing various fabrics. The food and cosmetic industries are also the major consumers of this dye. Besides, it is a valuable pH indicator for acid–base titrations because it gives yellow color in basic solution and red color in acidic solution. Wastewater released from various industries are highly colored due to the presence of the residual EO dye, and hence causes environmental and health problems. The literature review shows that the techniques available for the removal of EO dye from the wastewater are quite limited [2,3]. Additionally, these procedures are expensive and produce large amounts of sludge, and cannot be used by small industries to treat the wide range of EO dye present in wastewater. Alternatively, oxidative decolorization is a simple, efficient, and inexpensive method for the removal of dyes without introducing any impurities.

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N-haloarenesulfonamidates, generally known as organic *N*-haloamines, are mild oxidants containing a strongly polarized *N*-bonded halogen in its +1 oxidation state. Kinetics and mechanism of oxidation by these reagents have attracted the attention of many researchers, particularly synthetic and kinetic chemists due to their ability to act as sources of halonium cations, hypochlorite species and *N*-anions [4]. As a result, they interact with a wide range of functional groups effectively an array of molecular transformations [5,6]. Sodium *N*-chloro-p-toluenesulfonamide (chloramine-T; CAT) is a very important member of this class of compounds. It is a well-known oxidizing/analytical reagent and the kinetic and mechanistic aspects of many of its reactions have been well documented [5–11]. A perusal of literature indicates that the reports on the oxidation of dyes with this reagent are relatively sparse from its kinetic and mechanistic stand point [8,9]. Further, CAT is commercially available, cost effective, water tolerant, non-toxic, and easy to handle [11]. Hence, CAT has been used as an oxidant in the present case.

Our preliminary kinetic studies revealed that the EO dye decolorization with CAT is most effective in acidic conditions and decolorizes within 60 min. Consequently, we have established the optimum conditions for the facile oxidative decolorization of EO dye with CAT in acid medium. The other aim of this study is to unfold the mechanistic chemistry of this redox system kinetically, and also to deduce the kinetic modeling for the reaction.

2. Materials and methods

2.1. Materials

CAT (Merck) was purified by the method of Morris et al. [12]. An aqueous solution of CAT was prepared afresh whenever required, standardized iodometrically, and stored in brown bottles until further use to prevent its any photochemical deterioration. The concentration of stock solution was periodically checked by iodometric method. EO (Spectrochem Pvt. Ltd. Mumbai, India) was used as received and an aqueous solution of the desired strength of the dye was prepared afresh each time. All the other chemicals used were of analytical reagent grade and used as such. The real wastewater was collected from Mahaveera dyeing center and chemicals, Doddaballapur, Karnataka, India. Double-distilled water was used throughout this work.

2.2. Kinetic procedure

Kinetic runs were carried out using a UV–visible spectrophotometer (Digital spectrophotometer 166, Systronics, India). In the present study, the kinetic experiments were performed between 293 and 313 K. For this purpose, a Raaga Ultra Cold chamber with digital temperature control (India) was used. A constant temperature was maintained with an accuracy of ±0.1 °C. Detailed kinetic runs were performed under pseudo-first-order conditions of $[\text{oxidant}]_o >> [\text{dye}]_o$ at constant concentration of $HClO_4$ at 303 K. Reactions were carried out in glass stoppard Pyrex boiling tubes whose outer surface was coated black to eliminate any photochemical effects. The oxidant as well as requisite amounts of dye, $HClO_4$ solutions and water (to keep the total volume constant for all the runs) were taken in separate tubes and were thermostated at 303 K for 30 min. The reaction was initiated by the rapid addition of a measured amount of oxidant to the stirred reaction mixture. Immediately, 4 ml aliquot of the solution was pipetted into a cuvette and placed it in the spectrophotometer. Absorbance measurements were made at 474 nm (λ_{max} of the dye) for nearly three half-lives. The absorbance readings at $t = 0$ and $t = t$ are D_o and D_t, respectively. Plots of log D_o/D_t vs. time were made to evaluate the pseudo-first-order rate constants ($k' s^{-1}$) which were reproducible within ±5%. Rate constants reported are the mean values of duplicate kinetic runs. Regression coefficients (R^2) for all the linear lines were calculated using fx-100 W scientific calculator.

2.3. Reaction stoichiometry

The stoichiometry of the reaction was determined by equilibrating varying ratios of $[CAT]_o$ and $[EO]_o$ in presence of 4.0×10^{-3} M $HClO_4$ at 303 K for 24 h, and then determining the unreacted oxidant. The stoichiometric results obtained indicate that one mole of EO required one mole of CAT for oxidation as shown in Fig. 1.

2.4. Product characterization

The reaction mixture in the stoichiometric ratio was allowed to progress in presence of $HClO_4$ for about 24 h at 303 K under stirred conditions. After the completion of the reaction (monitored by TLC), the reaction products were neutralized with dilute NaOH and extracted with ethyl acetate. The organic products were identified as *N*-(4-diethylamino-phenyl)-hydroxyamine and 4-nitroso-benzenesulfonic acid. These products were separated by column chromatography and confirmed by GC-MS analysis. The mass spectra showed a molecular ion peak at 180 and 187 amu, clearly conforming *N*-(4-diethylamino-phenyl)-hydroxyamine and 4-nitroso-benzenesulfonic acid,

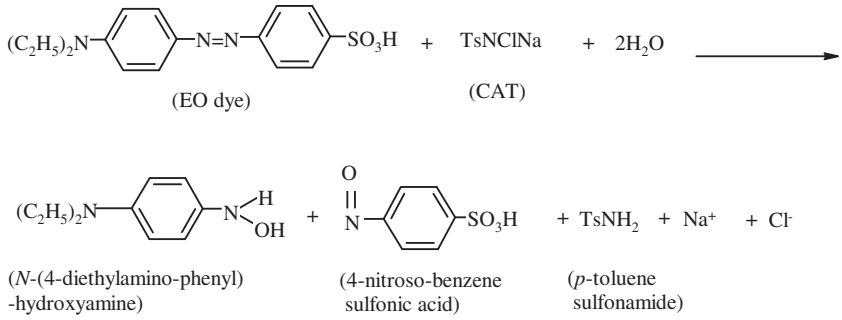

Fig. 1. Reaction stoichiometry (Here Ts = $CH_3C_6H_4SO_2-$).

respectively (Figs. 2 and 3). The reduction product of CAT, *p*-toluenesulfonamide (PTS or $TsNH_2$), was extracted with ethyl acetate and detected by paper chromatography [9] using benzyl alcohol saturated with H_2O as the solvent, with 0.5% vanillin in 1% HCl solution in EtOH as the spray reagent (R_f = 0.905).

3. Results and discussion

The kinetics of oxidative decolorization of EO with CAT was investigated at several initial concentrations of reactants in $HClO_4$ medium. All the kinetic runs were performed under pseudo-first-order conditions of $[CAT]_o >> [EO]_o$ at 303 K in presence of 4.0×10^{-3} M $HClO_4$. Under these conditions, the $[EO]_o$ was varied and plots of log (absorbance) or log (D_o/D_t) vs. time were linear ($R^2 > 0.9936$), indicating a first-order dependence of rate on $[EO]_o$. The pseudo-first-order rate constants ($k's^{-1}$) given in (Table 1), were found to be independent of $[EO]_o$, confirming the first-order dependence of rate on $[EO]_o$. Under the conditions of

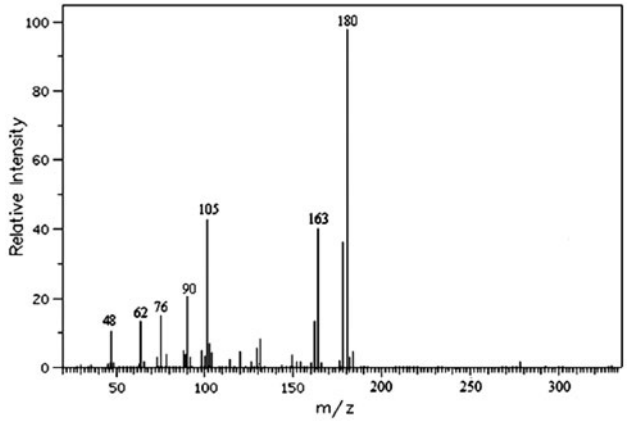

Fig. 2. GC-Mass Spectrum of *N*-(4-diethylamino-phenyl)-hydroxyamine with its parent molecular ion peak at 180 amu.

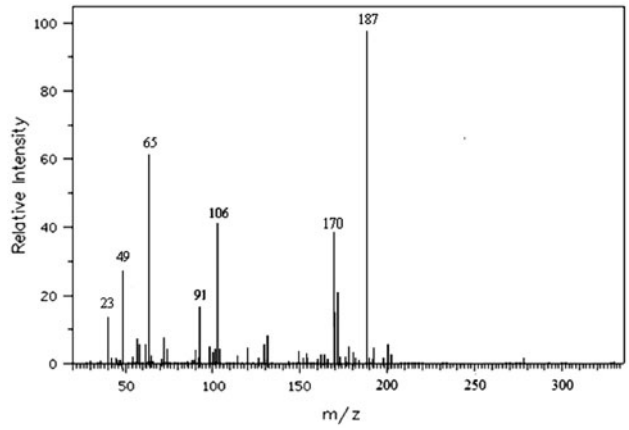

Fig. 3. GC-Mass Spectrum of 4-nitroso-benzenesulfonic acid with its parent molecular ion peak at 187 amu.

$[EO]_o = 3.0 \times 10^{-4}$ M, $[HClO_4] = 4.0 \times 10^{-3}$ M and at T = 303 K, an increase in $[CAT]_o$ increased the k' values (Table 1) and a plot of log k' vs. log [CAT] gave a straight line ($R^2 = 0.9875$) with a slope of 0.80, suggesting a fractional-order dependence of rate on $[CAT]_o$. Further, a plot of k' vs. [CAT] was also linear (R^2 = 0.9907), with a y-intercept, confirming the fractional-order dependence of rate on $[CAT]_o$.

At constant $[CAT]_o = 8.0 \times 10^{-3}$ M; $[EO]_o = 3.0 \times 10^{-4}$ M and at T = 303 K, the rate of reaction increased with increase in $[HClO_4]$ (Table 1). A plot of log k' vs. $[H^+]$ was linear (R^2 = 0.9989) with a slope of 0.84 indicates a fractional-order dependence on $[H^+]$. Further, a plot of k' vs. $[H^+]$ was linear (R^2= 0.9959) with a *y*-intercept corresponding to the rate law of the type = $a + b$ $[H^+]$. Further, the wastewater from various industries contains different pH values and the pH is an important parameter in the efficiency of the dye decolorization process. Hence, the effect of pH on decolorization rate was studied at various pH values ranging from 1 to 10 with all other experimental conditions being held constant. It was observed that the rate of decolorization of EO dye increased with pH. The decolorization rate

Table 1
Influence of [EO], [CAT], and [$HClO_4$] on the reaction rate at 303 K

10^4 [E O]$_o$ M	10^3 [CAT]$_o$ M	10^3 [$HClO_4$] M	10^4 k' (s^{-1}) M
0.5	8.0	4.0	3.85
2.0	8.0	4.0	4.15
3.0	8.0	4.0	4.27
6.0	8.0	4.0	4.47
8.0	8.0	4.0	4.84
3.0	2.0	4.0	1.40
3.0	4.0	4.0	3.05
3.0	8.0	4.0	4.27
3.0	10.0	4.0	5.30
3.0	12.0	4.0	6.40
3.0	8.0	1.0	1.20
3.0	8.0	2.0	2.30
3.0	8.0	4.0	4.27
3.0	8.0	6.0	5.90
3.0	8.0	8.0	7.23

constants k' (10^4 s^{-1}) determined at pH of 1.0, 2.0, 3.0, 4.0, 6.0, 8.0, and 10.0 were 10.3, 7.23, 1.21, 0.85, 0.41, 0.20, and 0.08, respectively. The decolorization rates are high at lower pH and very low at higher pH. Hence, it is very difficult to study the kinetics of variation of CAT, EO, $HClO_4$ concentrations, and temperature at higher and lower pH. Consequently, in the present study, the pH of the solution was maintained at pH 2.39 ([$HClO_4$] = 4.0×10^{-3} M) and detailed kinetic runs were carried out. Keeping pH 2.39 is only for experimental convenience.

In order to find out the nature of reactive species, the dielectric constant (D) of the medium was varied by adding MeOH (0–30% v/v) to the reaction mixture. The rate constants 10^4 (k' s^{-1}) determined at D values of 76.73, 72.37, 67.48, and 62.71 were 4.27, 4.95, 5.87, and 7.10, respectively. The values of dielectric constant of MeOH–H_2O mixtures reported in the literature were used [13]. A plot of log k' vs. 1/D was linear (R^2 = 0.9990) with a positive slope. The reaction rate was studied at different temperatures and activation parameters for the overall reaction have been computed using the Arrehenius plot of log k' vs. 1/T (R^2 = 0.9939). These data are summarized in Table 2. The rate remained constant with the addition of Cl^- or Br^- ions in the form of NaCl or NaBr (2.0×10^{-2} to 8.0×10^{-2} M). This indicates that the halide ions play no role in the reaction. Addition of the reduction product of CAT, *p*-toulenesulfonamide or $TsNH_2$ (1.0×10^{-3} to 6.0×10^{-3} M) to the reaction mixture did not bring about significant change in the rate of the reaction, indicating that it is not involved in a pre-equilibrium to the rate-determining step (rds) of the reaction scheme. The influence of ionic strength on the reaction rate was studied by adding 0.3 M $NaClO_4$ solution to the reaction mixture. It was found that the ionic strength has negligible effect on the reaction rate. Hence, no attempt was made to keep the ionic strength of the medium constant during the kinetic runs. Addition of reaction mixture to aqueous acrylamide solution did not initiate polymerization showing the absence of free radical species.

Table 2
Influence of temperature on the reaction rate and activation parameters for the oxidative decolorization of EO dye with CAT in acid medium

Temperature (K)	10^4 k' (s^{-1})
293	2.12
298	3.26
303	4.27
308	5.33
313	8.63
E_a (kJ mol^{-1})	58.9 ± 0.02
$\Delta H^{\neq}$ (kJ mol^{-1})	56.3 ± 0.01
$\Delta G^{\neq}$ (kJ mol^{-1})	101 ± 0.20
$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	−146 ± 0.01

Note: [CAT]$_o$ = 8.0×10^{-3} M; [EO]$_o$ = 3.0×10^{-4} M; [$HClO_4$]$_o$ = 4.0×10^{-3} M.

CAT (TsNClNa) behaves like a strong electrolyte [14] in aqueous solution and the anion is protonated in acidic solutions to give the free acid TsNHCl. The free acid then either disproportionates to give dichloramine-T ($TsNCl_2$) and p-toluenesulfonamide ($TsNH_2$) or hydrolyses to give hypochlorous acid (HOCl) and $TsNH_2$. HOCl further protonates to give H_2O^+Cl. Therefore, the possible oxidizing species in acidified CAT solutions are TsNHCl, $TsNCl_2$, HOCl and probably H_2O^+Cl [12,14,15]. If $TsNCl_2$ were to be the reactive species, then the rate law predicts a second-order dependence of rate on [CAT], which is contrary to experimental evidences. If HOCl is primarily involved, a retardation of rate by the added *p*-toluenesulfonamide is expected. However, no such effect was noticed. Bishop and Jennings [14] have made detailed calculations on the concentration dependence of various species of CAT at different pH and shows that TsNHCl is the most effective oxidizing species in acid medium. Further, in the present case, the order with respect to [H^+] is fractional which signifies that the EO dye protonates as shown in Fig. 4. Based on the above facts and experimental results, Fig. 4 (reaction scheme) can be formulated to account the experimental results.

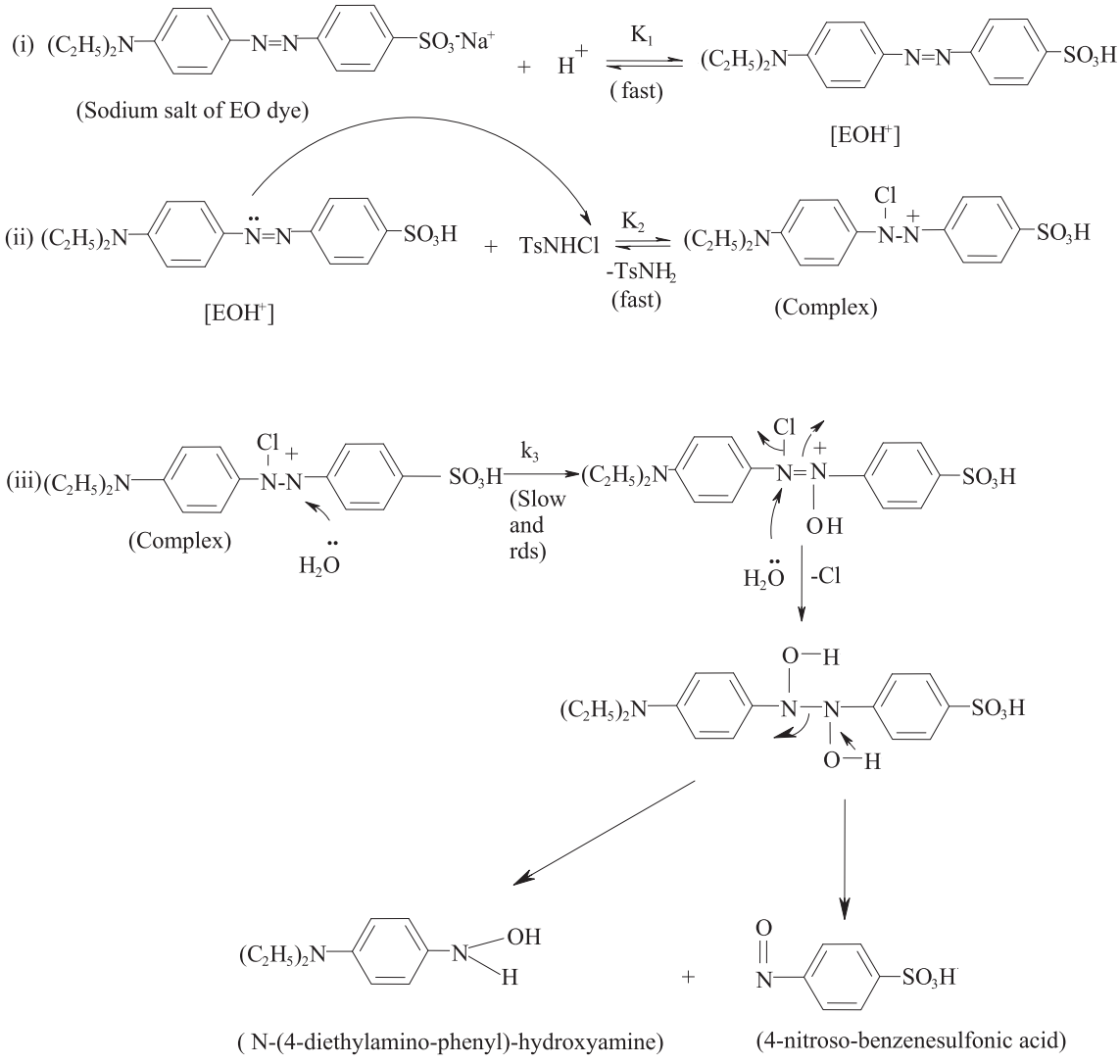

Fig. 4. A detailed mechanistic scheme for oxidative decolorization of EO dye with CAT in acid medium.

In a fast pre-equilibrium step (step (i) of Fig. 4), in acid medium, the sodium salt of EO dye gets protonated to form the protonated EO dye (EOH^+), which is the reactive substrate species involved in the reaction. In the next fast equilibrium step (step (ii)), a lone pair of electrons present on the nitrogen atom of the protonated dye attacks the positive chlorine of the conjugate acid (TsNHCl) of CAT to form an intermediate complex with the elimination of $TsNH_2$. This complex in a slow and rate-determining step, undergoes hydrolysis followed by several fast steps, leading to the formation of the ultimate products *N*-(4-diethylamino-phenyl)-hydroxyamine and 4-nitroso-benzenesulfonic acid.

The rate law for Fig. 4 can be deduced as follows:

If $[EO]_T$ is the total effective concentration of [EO], then

$$[EO]_T = [EO] + [EOH^+] + [Complex] \quad (1)$$

From step (i) of Fig. 4,

$$[EO] = \frac{[EOH^+]}{K_1 H^+} \quad (2)$$

From step (ii) of Fig. 4,

$$[EOH^+] = \frac{[Complex]}{K_2\,[TsNHCl]} \quad (3)$$

By substituting [EOH^+] from Eq. (3) into Eq. (2), one obtains

$$[EO] = \frac{[Complex]}{K_1K_2\,[TsNHCl][H^+]} \tag{4}$$

By substituting [EOH^+] and [EO] from Eqs. (3) and (4), respectively, into Eq. (1), and solving for [Complex], we get

$$[Complex] = \frac{K_1K_2\,[TsNHCl][H^+][EO]_T}{1 + K_1\,[H^+] + K_1K_2\,[CAT][H^+]} \tag{5}$$

From slow and rate-determining step (step (iii)) of Fig. 4,

$$Rate = k_3\,[complex] \tag{6}$$

By substituting [Complex] from Eq. (5) into Eq. (6), the following rate law is obtained,

$$Rate = \frac{K_1K_2k_3[TsNHCl][EO]_T[H^+]}{1 + K_1\,[H^+] + K_1K_2\,[CAT][H^+]} \tag{7}$$

Since the absorbance corresponds to both CAT and TsNHCl, and CAT is consumed only in the formation of TsNHCl, we can write Eq. (7) as

$$Rate = \frac{K_1K_2k_3[CAT][EO]_T[H^+]}{1 + K_1\,[H^+] + K_1K_2\,[CAT][H^+]} \tag{8}$$

Rate law (8) predicts the first-order dependence of rate on $[EO]_o$ and fractional-order dependence on both $[CAT]_o$ and $[H^+]$, which is in agreement with our experimental results.

Since, Rate = $k'\,[EO]_t$, then Eq. (8) becomes

$$k' = \frac{K_1K_2k_3[CAT][H^+]}{1 + K_1\,[H^+] + K_1K_2\,[CAT][H^+]} \tag{9}$$

$$\frac{1}{k'} = \frac{1}{K_1K_2k_3[CAT][H^+]} + \frac{1}{K_2k_3[CAT]} + \frac{1}{k_3} \tag{10}$$

According to Eq. (10), double-reciprocal plots of $1/k'$ vs. 1/[CAT], (Fig. 5, supplementary material) and $1/k'$ vs. $1/[H^+]$ (Fig. 6, supplementary material) were found to be linear ($R^2 > 0.9927$) with intercepts. From the slopes and intercepts of such plots, values of K_1, K_2, and k_3 were found to be 41.66 M^{-1}, 250 M^{-1}, and 2×10^{-3} s^{-1}, respectively. Fig. 4 (reaction scheme) and rate law (8) can explain the following observed experimental results.

The proposed reaction mechanism is also evinced by the observed zero effect of ionic strength on the rate of reaction. The primary salt effect on the reaction rates has been described by Bronsted and Bjerrum [16] theory. According to the concept of this theory, the effect of ionic strength (μ) on the rate of a reaction involving two ions is given by the relationship:

$$\log\ k' = \log\ k'_0 + 1.018Z_AZ_B\mu^{1/2} \tag{11}$$

where A and B are the reacting ions, Z_A and Z_B are the charges on the respective species, and k' and k'_o are the rate constants in the presence and in the absence of the added electrolyte, respectively. Eq. (11) shows that a plot of log k' vs. $\mu^{1/2}$ would be linear yielding a slope 1.018 Z_AZ_B and an intercept log k'_o. As the slope of the line depends on Z_AZ_B, i.e. charges of the reacting ions, three special cases may arise: (i) if A and B have the same charges, Z_AZ_B will be positive and the rate constant k' increases with $\mu^{1/2}$; (ii) if A and B have opposite signs, Z_AZ_B will be negative and the rate constant k' decreases with $\mu^{1/2}$; and (iii) if either A or B is uncharged, Z_AZ_B is equal to zero and k' is independent of the ionic strength of the solution. In the present case, plot of log k' vs. $\mu^{1/2}$ is a straight line with zero slope indicating that a neutral molecule is involved in the rate-determining step (step (iii) of Fig. 4). Hence, variation of the ionic strength of medium does not alter the rate and it clearly conforms to the above theory.

The rate of oxidation of EO dyes with CAT increases with decrease in polarity of solvent. In other words decrease in rate with increase in dielectric constant (D) is observed; this is due to polar character of transition state as compared to the reactant. The general equation relating D with the rate constant in a bimolecular reaction has been derived by Laidler and Landskroener [17]. Further Amis [18] has shown that

$$\log\ k'_D = \log\ k' + Ze\ \mu/2.303k\ Tr^2D \tag{12}$$

where k'_D is a function of dielectric constant D, Ze is the charge on the ion, μ is the dipole moment of the dipole, k is the Boltzmann constant, T is the absolute temperature, and r is the distance of approach between the ion and dipole. Eq. (12) predicts a linear relation between a negative ion and a dipole, while a positive slope is obtained for positive ion-dipole reactions. In the present study, a plot of log k' vs. 1/D is linear with a positive slope, thus supporting the

participation of a positive ion and dipole in the rate-determining step, as can be seen in Fig. 4.

The proposed mechanism is supported by the moderate values of energy of activation and other thermodynamic parameters. The positive values of $\Delta H^{\neq}$ and $\Delta G^{\neq}$ indicate that the transition state is highly solvated. The large negative values of $\Delta S^{\neq}$ suggest a more ordered activated complex. The ineffectiveness of *p*-toluenesulfonamide and halide ions and the rate of the reaction are in agreement with the proposed mechanism and the derived rate law, respectively. Stoichiometry of the reaction also supports the proposed mechanism.

We have also sought to make chemical oxygen demand (COD) for EO dye. It is a measure of oxidizable matter in dye stuff. The COD of EO dye was determined using standard dichroamte method. The procedure followed to determine COD value was according to a literature procedure [19]. Under the present experimental conditions, COD of EO dye sample was fond to be 1,033.6 mg/lit.

In industries, many organic and inorganic salts are commonly used as additives. In order to know the interference of salts on the present decolorization process, sodium salts of carbonate, sulfate, nitrate, and chloride were employed at different concentrations. The decolorization rate constants k' (10^4 s^{-1}) obtained at 0.01 M and 0.02 M of Cl^-, NO_3^{2-}, SO_4^{2-}, and CO_3^{2-} are 4.23 and 4.29, 3.26 and 3.00, 2.20 and 1.87, and 0.01 and 0.01, respectively. The rate of decolorization for the standard run is 4.27×10^{-4} s^{-1}. It is seen from the above values, the rate of nitrate and sulfate ions decrease the decolorization rate with the increase in their concentrations. On the other hand, chloride is not having any significant effect on the decolorization rate. In presence of carbonate ions, the rate of decolorization is almost zero.

In this research, an attempt has been made to develop optimum conditions for the oxidative decolorization of EO dye with CAT in acid medium. This redox system is simple, efficient, and inexpensive and has the potential to successfully remove EO dye present in wastewater. Hence, developed decolorization method is expected to be helpful to treat the EO dye present in industrial wastewater after suitable experimental modifications to minimize the toxicity caused by this dye. It means that the manipulation of concentrations of the reactants and acid, and temperature depend on the wastewater collected from different industries. The applicability of this method was tested with real water containing EO dye, which was collected from a dyeing industry. The water sample was filtered and was diluted to achieve the desired concentration. The developed technique was adopted with real water under identical set of experimental conditions (Table 1). The decolorization rate constant was found to be 2.30×10^{-4} s^{-1}. This value is quite agreeable to our standard run value (4.27×10^{-4} s^{-1}). It clearly justifies the use of the developed method to treat EO dye present in wastewater. Therefore, this method is a valuable addition to the existing method to treat EO dye present in industrial wastewater.

4. Conclusions

In the present research, we have developed a simple, efficient, and cost-effective oxidation process for the decolorization of EO dye with CAT in acid medium. A systematic kinetic and mechanistic study has also been performed for this redox system. The oxidation reaction obeys the rate law: rate = k $[CAT]^{0.80}[EO]^{1}$ $[H^+]^{0.84}$. Oxidation products of EO were identified as *N*-(4-diethylamino-phenyl)-hydroxyamine and 4-nitroso-benzenesulfonic acid by GC-MS analysis. Based on the kinetic results, suitable mechanism and related rate law have been worked out. This decolorization technique can be successfully employed to abolish EO dye present in industrial wastewater after suitable modifications.

Supplementary material

The supplementary material for this paper is available online at http://dx.doi.org/10.1080/19443994.2014.978388.

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